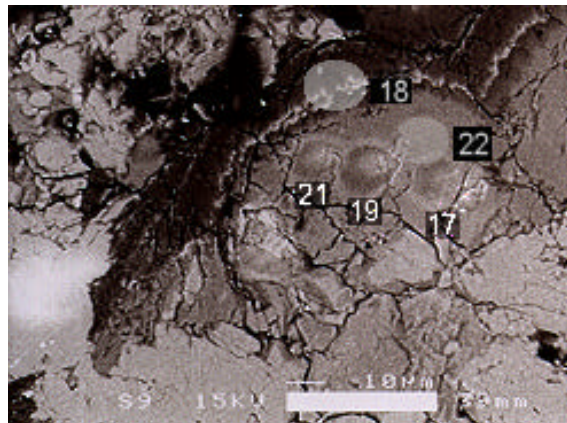


Oxygen isotope ratios of ALH84001 carbonates have been measured in-situ and with high spatial resolution, using an Isolab 54 ion microprobe¹. The immediate objectives of work, which is ongoing, is to search for and map any isotopic gradients which may exist within the carbonates. We hoped in doing this to address a number of questions: Is there evidence for isotopic exchange between the carbonate and surrounding pyroxene or maskelynite, such as might arise if the carbonates were deposited at high temperature? Are profiles related in a simple way to the carbonate chemistry, which would suggest that isotopic variations were a feature of the invading fluids? Alternatively, are variations between carbonate regions unrelated to chemical composition, which would suggest that oxygen isotope ratios were determined by localised interactions with the host rock? What are the implications of the variations for the temperature of deposition?

We studied a single grain mount of a sample from the 'crushed zone' of ALH84001. Most of the carbonate lies within a vein running across the sample, much of it showing the characteristic concentric zoning in backscattered electron images. Minor pockets of carbonate are found in pyroxene. EDX analyses confirm that the carbonate in our sample belongs to the same series of compositions as reported by other workers; however, we did not observe any ankeritic dolomite, presumably because our section does not expose any of the earliest deposited material.

The techniques used here were as reported previously^{1,8}: A caesium beam typically between 0.1–0.3nA focused to a spot ~10µm in diameter was used to sputter secondary ions from the sample. These were mass analysed and detected in the Isolab 54 ion probe using a Faraday collector for the $^{16}\text{O}^-$ ions and a CDS detector for the $^{18}\text{O}^-$ ions¹. Magnesite, calcite and siderite standards were used for calibration. We observed no significant (<1‰) matrix effect between magnesite and siderite, but a large matrix effect (approx 18‰) between siderite/magnesite and calcite. Measurements of ankerite and dolomite will be carried out to characterise the matrix effect further. All the data here have been normalized to siderite/magnesite, and for now a fixed correction of -2‰ has been applied to allow for the small Ca content of the ALH84001 carbonate. Con-

fidence levels in the quoted absolute $\delta^{18}\text{O}$ values are $\pm 2\%$.

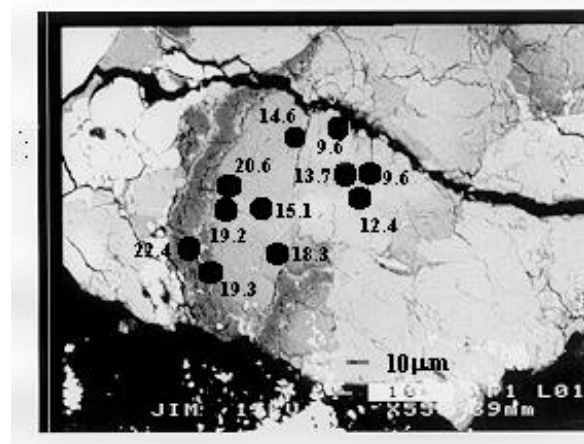


We previously reported analyses of $^{18}\text{O}/^{16}\text{O}$ ratios in a carbonate rosette⁷ which showed an apparent gradient in $^{18}\text{O}/^{16}\text{O}$ from +21‰ (SMOW) near the outer rim of the rosette to +17‰ (SMOW) in the interior. These data, together with a further two analyses, are shown in figure 1.

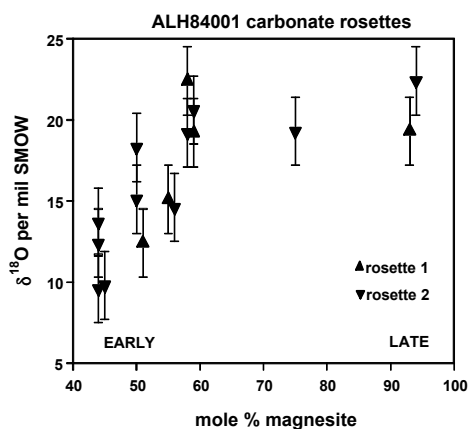
We have since studied a second carbonate rosette, which shows a slightly wider range of compositions in its core than that in figure 1; the most Fe-rich carbonate is approx. $\text{Mg}_{44}\text{Ca}_{17}\text{Sd}_{39}$. The oxygen isotope analyses of this rosette are shown in figure 2, which is a backscatter electron photograph onto which the positions of the ion beam burn marks and their measured $\delta^{18}\text{O}$ values have been added schematically. The ion probe crater diameter is about 10 microns. $\delta^{18}\text{O}$ values range from 10 to 22‰, and also appear to show an isotopic gradient between the outer and inner parts of the rosette.

Previous $^{18}\text{O}/^{16}\text{O}$ measurements have been reported using acid dissolution⁴ or ion probes^{8,9}, but have been used to reach conflicting conclusions concerning the formation temperature and origin of the carbonates. Romanek et al⁴ measured three $\delta^{18}\text{O}$ values using stepped acid dissolution of carbonate rosettes, from which they inferred end-member values of +13.3‰ and +22.3‰ for the inner (Ca-Fe rich) zones and outer (Mg-rich) rims respectively. Ion probe measurements have reported a somewhat larger range of values. Leshin et al⁸, reported values between +5.6‰ and +21.6‰ whilst Valley et al⁹ reported values ranging between 9.5‰ to 20.6‰. Leshin et al interpret their data as being consistent with partial high temperature equilibration with

neighbouring pyroxene whereas Valley et al interpret their data as being consistent with low temperature deposition. In our previously reported measurements⁷, we argued that the high $\delta^{18}\text{O}$ values for the carbonate obtained by us and others could not be used to exclude a high temperature origin of the carbonate rosettes, only that carbon dioxide which formed the rosettes must have been in contact with water at low temperature ($<100^\circ\text{C}$) at some time in its history but not necessarily during formation of the rosettes.



. In figure 3, the $\delta^{18}\text{O}$ values for both rosettes are plotted against mole% magnesite. There appears to be a consistent trend, with low values, around 12‰, for the inner (early), less magnesium rich cores and high values, around 20‰, for the (later) more magnesium rich carbonate.



This observation is in good agreement with the data published by Romanek et al⁴, obtained by acid dissolution, and with the range of values obtained using an ion probe by Valley et al⁸, although

Valley et al. reported that there was no apparent correlation between their measured $\delta^{18}\text{O}$ values and chemical composition. Unlike Leshin et al⁹, we see no carbonate that is in equilibrium with the bulk minerals in ALH84001. However none of our sections so far analyzed have dolomite-rich cores¹⁰, presumably due to polishing not having exposed the small cores. It is certainly plausible that continuation of the trend of figure 4 to more magnesite poor values would be consistent with the presence of lower $\delta^{18}\text{O}$.

As with earlier oxygen isotope analyses, our data is open to a number of interpretations. Nevertheless some constraints on acceptable models can be made, particularly in view of the apparent systematic variation in $\delta^{18}\text{O}$ across the carbonate. This variation could arise as a result of a change (reduction) in the temperature of the fluid with time along the lines suggested by Romanek et al⁴. If this is the case, the lower $\delta^{18}\text{O}$ values observed by Leshin et al⁹ in the cores, and the trend suggested by figure 3, imply that the early fluids were hotter than those proposed by Romanek et al⁴. An alternative is that figure 3 represents a change in the isotopic and chemical composition of the fluid, rather than temperature, i.e. the changes reflect some external process. Where the isotopic exchanges took place which caused the variations in $\delta^{18}\text{O}$ is also not clear from our data, which is currently based on just two rosettes. If figure 3 is representative of all the carbonates, the isotopic composition could have been acquired by exchange between fluid and rock over a wide area. If as suggested by Valley et al⁸, there is a wide variation in $\delta^{18}\text{O}$ between rosettes, these $\delta^{18}\text{O}$ values must have been acquired as a result of very localized interactions.

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